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(71) Applicants
Varian Associates, Inc., 611 Hansen Way, Palo Alto, California 94303, United States of America
(72) Inventor
Ahmad Abu-Shumays
(74) Agents
A. Poole & Co., 54 New Cavendish Street, London W1M 8HP

(54) Multiple-wavelength spectrophotometer

(57) Apparatus for spectrophotometric analysis of a plurality of discrete wavelength intervals includes a polychromatic light source 10, a dispersive element such as a concave grating polychromator 18 for analyzing the light into desired wavelength constituents, a corresponding plurality of exit slits 22*a*, 22*b* . . . for transmitting said wavelength constituents for illuminating a single detector 32 and a rotating chopper 24 with apertures 28*a*, 28*b* . . . distributed to uncover a single one of the exit slits at a time during rotation of the chopper.

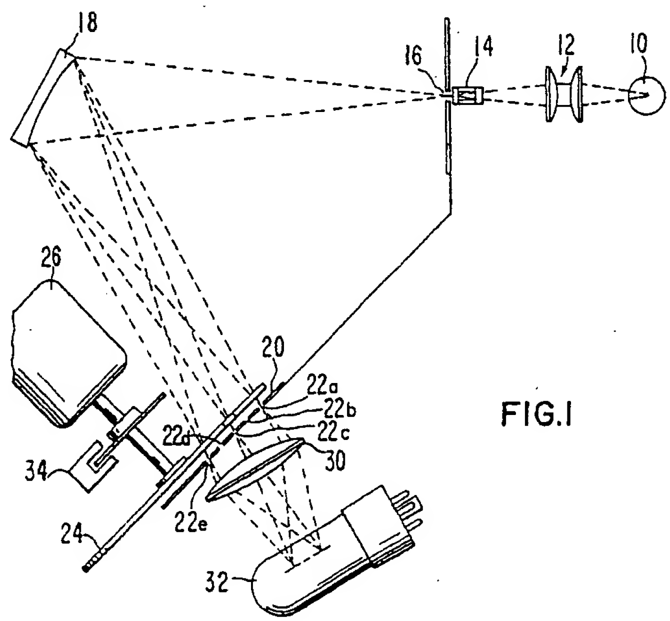

FIG.1

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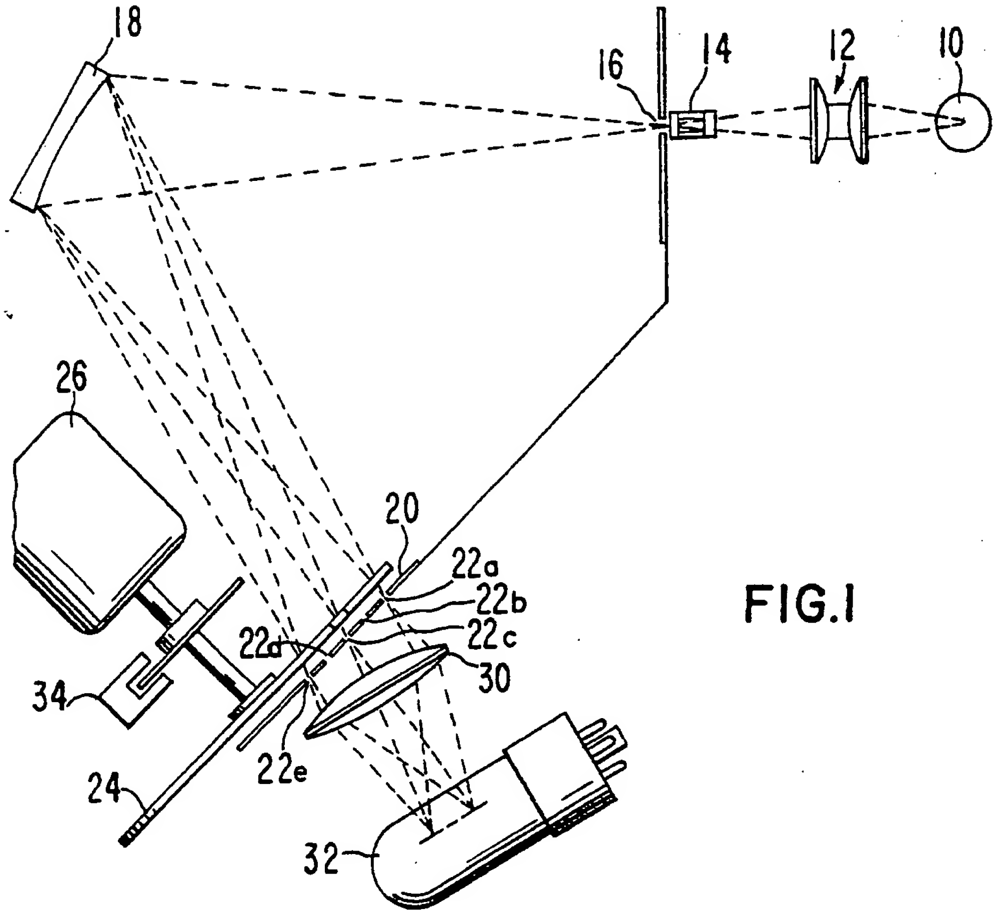


FIG.1

FIG.2

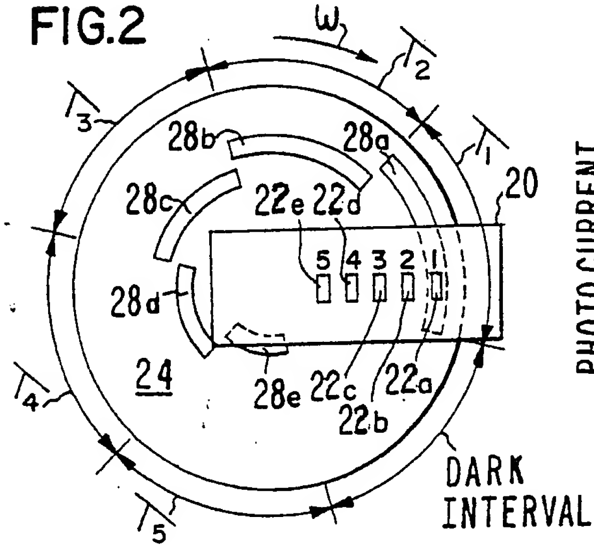


FIG.3

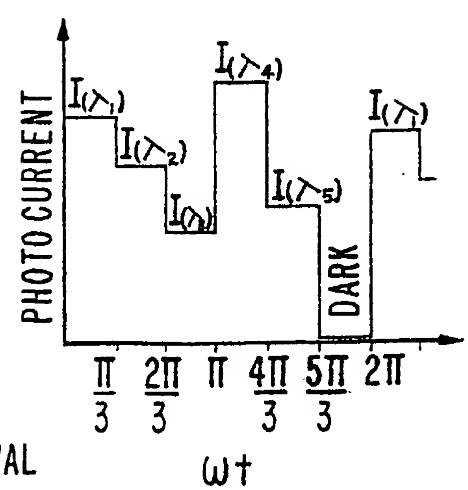


FIG.4

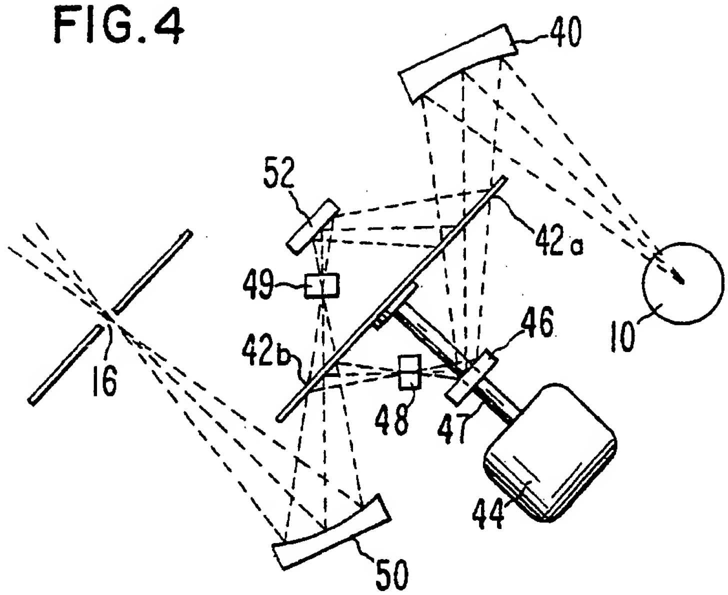
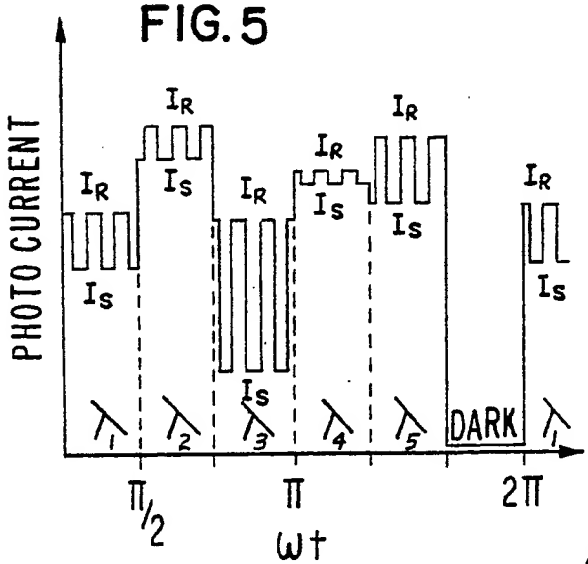


FIG.5



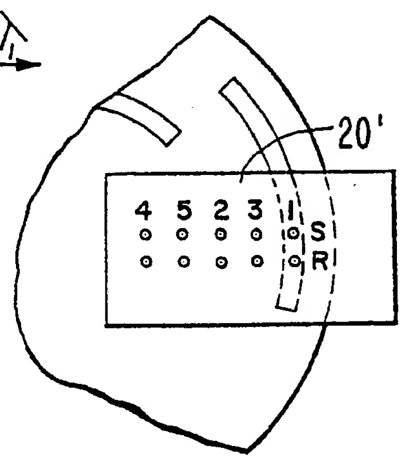


FIG.6

FIG.7

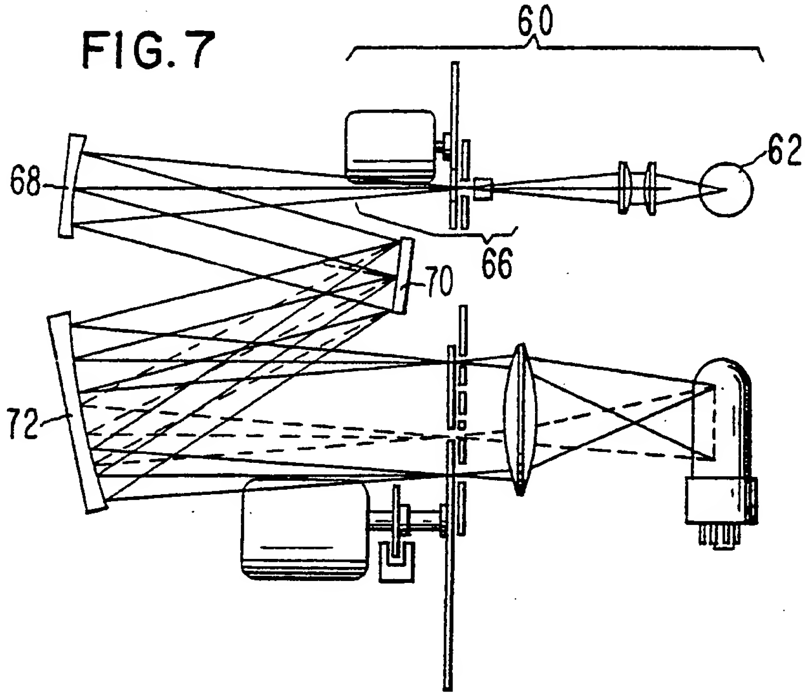
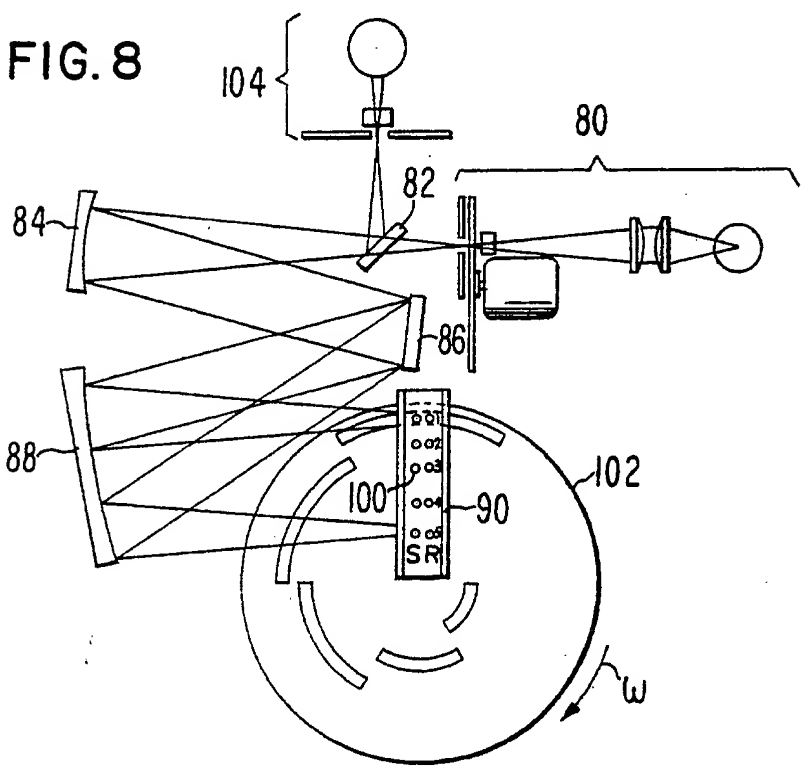


FIG.8



SPECIFICATION

Multiple-wavelength spectrophotometer

Technical Field

The present invention pertains to spectrophotometric instrumentation and in particular to analyses of multiple discrete spectral regions.

Background Art

Many analytical methods require photometric measurement at a number of wavelength intervals. The data acquisition time is necessarily quite short when continuous real time absorption measurements are performed upon a flowing liquid for example. One specific example of such requirements are the absorbance measurements on the eluant of a liquid chromatographic apparatus.

Generally the prior art instruments may be classified in two major groups. First are those instruments based upon a rapid-scan monochromator which sweeps through the region of spectral interest. The scanned monochromatic radiation transmitted through the sample impinges a suitable detector. With such an instrument, measurements required at a small number of predetermined wavelength intervals incur the time delay imposed by the monochromator scanning rate between such desired wavelength intervals.

The second class of instruments employs a polychromatic source with analyses yielding a number of discrete wavelength intervals available at respective exit apertures. An array of optical detectors each dedicated to respective wavelength intervals provides the required photometric data. Such a system exhibits good relative and absolute sensitivity because of the parallel data acquisition in the several wavelength intervals. However, such an instrument is complex and costly owing in part to redundancy of the components. Separate detectors for closely spaced wavelengths of interest are also a source of design difficulty.

Brief Summary of the Invention

It is an object of the invention to provide inexpensive apparatus for rapid photometric analysis of a sample over a small number of discrete wavelength intervals.

In one feature of the present invention, the grating polychromator illuminates a set of slits for selecting the corresponding desired wavelength intervals.

In another feature of the invention, a first rotating chopper uncovers the exit slits sequentially for transmission therethrough to illuminate a single photodetector.

In another feature of the invention, a second rotating chopper is provided to alternately direct the incident polychromatic radiation to a sample cell and a reference cell, subsequently directing said sample cell and reference cell transmission radiation to follow a common optical path for subsequent analysis.

In another embodiment of the invention, retro-reflective means are provided for redirecting the sequentially transmitted wavelength intervals back over the optical path to a splitter which directs such reflected radiation to said single photodetector.

Brief Description of the Drawings

Figure 1 schematically illustrates a preferred optical system of the present invention.

Figure 2 shows the chopper of Figure 1.

Figure 3 is an illustration of the waveform obtained with the system of Figures 1 and 2.

Figure 4 illustrates a double beam system.

Figure 5 illustrates the waveform obtained with the system of Figure 4.

Figure 6 shows an aperture plate for the embodiment of Figures 4 and 1.

Figure 7 shows another embodiment.

Figure 8 shows a zero dispersion embodiment.

Detailed Description of the Invention

Referring now to Figure 1, there is shown a schematic illustration of the preferred optical system. A suitable light source 10 as, for example, a D2 lamp, is collimated and focused by lens pair 12 through sample cell 14 at the entrance slit 16. The transmitted light falls on analyzer 18, preferably a concave grating. Light of various wavelengths, dispersed through respective angles, is transmitted through the exit plane of slit defining plate 20 at slit positions 22*a*, 22*b*, 22*c* .... Only one of these slits is uncovered at a time by apertures provided in chopper 24 driven by motor 26. Chopper 24 is more clearly shown in Figure 2 to be divided into a number of angular intervals or sectors each providing an aperture which illuminates a respective slit 22*a*, 22*b*, ... when the corresponding aperture 28*a*, 28*b* ... is aligned therewith. One sector, without an aperture located therein provides a dark current background sample. Motor 26 is energized to rotate chopper 24 at a uniform angular velocity ω. The light emerging from respective slits 22 is focused by lens 30 onto the photocathode of detector 32, for example, a photomultiplier.

The time dependence of the photocurrent derived from detector 32 consists of a series of non-overlapping rectangular pulses, each corresponding to a given wavelength and bearing fixed phase relation to pulse patterns corresponding to other wavelengths. The decoding or separation of these pulse trains is aided by an indexing signal derived from a key-generator coupled to a rotating chopper disc. A representative waveform of Figure 3 results from the above-described arrangement. An indexing signal derived from index generator 34 is available for synchronizing the successive waveform samples in appropriate circuitry. The processing of such data is outside the scope of the present invention and is not discussed further.

In the apparatus as above described, one of the wavelength intervals can be chosen to serve as

reference. In Figure 4, there is illustrated a double-beam system for alternate transmission of the incident polychromatic light through sample and reference cells. The substitution of this apparatus for the corresponding components of the apparatus of Figure 1 is straightforward. In this double beam system the light from lamp 10 falls on mirror 40 which directs the light to portion 42*a* of rotating chopper 42. Light transmitted through the chopper portion is reflected from an annular mirror 46 which surrounds the chopper shaft 47. The light reflected from mirror 46 is transmitted through reference cell 48 where it is now reflected from portion 42*b* of chopper 42 to another focusing mirror 50 and directed to a crossover at entrance slit 16. Light reflected by chopper portion 42*a* is directed to mirror 52 symmetrically disposed with respect to mirror 46 and the plane of chopper 42. Reflected light from mirror 52 is brought to a focus within and transmitted by sample cell 49. Light incident on chopper portion 42*b* from sample cell 49 is alternately transmitted by such chopper portion with respect to light transmitted by reference cell 48. The sample cell transmitted light, when transmitted by chopper portion 42*b* strikes focusing mirror 50 in a common path with the reference cell transmitted light. Thus the system of Figure 1 from entrance slit 16 forward along the optical path transmits alternate sample cell and reference cell absorbance fluxes resulting in a waveform such as shown in Figure 5. Such a system preferably employs small circular apertures such as shown in Figure 6 wherein the dual slit defining plate 20 is replaced by plate 20′ and each of the slits 22*a*, 22*b* . . . are replaced by the pair of apertures 22*Sa* and 22*Ra*; 22*Sb* and 22*Rb*; . . . 22*Se* and 22*Re*. The respective *S* (Sample) and *R* (Reference) apertures are sufficiently small and sufficiently displaced in angle to transmit only the sample or reference cell light respectively at any one time. It will be seen that motor 44 driving chopper 42 is to be synchronized with motor 26 according to the number of repetitions of sample and reference desired for each wavelength. Thus, for one sample-reference pair per wavelength and for a six-sector chopper, motor 44 operates at a rotational frequency of 6ω (where ω is the frequency of chopper 24). For n sample-reference pairs chopper 44 must operate at $6n\omega$.

Figure 7 shows an embodiment similar to that of Fig. 1. A sample-reference chopper 60 comprises light source 62, optical elements 64 and a sample-reference sequencing selector 66. The latter may take the form of Fig. 2, or any suitable design known for the purpose of illuminating sample and reference cells with known relative intensity at any given wavelength. For convenience, however, only a single cell is indicated. Spherical mirror 68 directs the transmitted light to dispersive element 70 and thence to spherical mirror 78. Dispersive element 70 may be either a plane grating or prism. The choice of a prism for dispersive element 70 allows a higher efficiency for operation in the ultraviolet. The choice of a prism also reduces spectral complexities which may be introduced by higher order grating spectra. The light reflected from spherical mirror 78 is thence directed to a subsystem 74 comprising wavelength chopper optics and detector in connection with Fig. 1. This subsystem 74 is substantially as described above.

Yet another embodiment is shown in Fig. 8 which comprises a zero dispersion system wherein the multiple wavelengths are selected at an intermediate position by a set of respective retro-reflectors in a manner similar to that described for the previous embodiments. The selected wavelengths are sequentially reflected back through the monochromator and emerge through a single fixed exit slit providing a relatively small image on the detector photocathode. One can combine with this a system such as that of Fig. 4 to accomplish a dual cell arrangement at the entrance or exit slit of the monochromator.

Since many changes could be made in the above-described construction and many apparently widely differing embodiments of this invention could be made without departing from the scope thereof, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not a limiting sense.

CLAIMS

1. Spectrophotometric apparatus for obtaining substantially simultaneously a plurality of absorbance measurements at a corresponding plurality of wavelengths from a sample, comprising:

sample cell means adapted to transmit light therethrough;

polychromatic light source means for transmission of a portion of light from said source at a plurality of wavelengths through said sample cell means;

dispersive means for analysis of said polychromatic light transmitted by said sample cell means into a plurality of wavelength constituents;

aperture means and means for transmitting sequentially selected said wavelength constituents through said aperture means;

single detector means responsive to said selected wavelength constituents transmitted through said aperture means for generating a time dependent signal containing the absorbance information for each said wavelength constituent transmitted through said sample cell means;

means for extracting from said time dependence of said signal said absorbance information for each said wavelength constituent; and

means for recording said data.

2. The apparatus of claim 1 further comprising means for directing another portion of light from said light source means through another sample cell means and means for sequentially presenting said portion and said another portion to said dispersing means.

3. The apparatus of claim 2 further comprising means for comparing a portion of said time-dependent signal of said portion of light transmitted through said sample corresponding to one said selected wavelength constituent cell means with another portion of said time-dependent signal corresponding to one said selected wavelength constituent of said another portion of light transmitted through said another sample cell means.

4. The apparatus of claim 3 including comparison means for comparing said portion of said time-dependent signal with said another portion of said time-dependent signal whereby a sample reference comparison is achieved.

5. A rotating chopper for sequentially transmitting selected portions of incident light comprising:

rotating mask means and means for establishing said rotation;

a plurality of sector portions in said rotating mask means, said portions each comprising an arcuate aperture segment having a radial position, a radial width and angular length, and fixed mask means comprising a narrow slit extending radially for transmitting light from any of said openings in said rotating mask means;

single detector means for generating a signal in response to light transmitted from said apertures; and

optical focusing means for focusing light from said plurality of radial positions upon said detector means.

6. Spectrophotometric apparatus for obtaining substantially simultaneously a plurality of absorbance measurements at a corresponding plurality of wavelengths from a sample, comprising:

sample cell means adapted to transmit light therethrough;

polychromatic light source means for transmission of a portion of light from said source at a plurality of wavelengths through said sample cell means;

dispersive means for analysis of said polychromatic light transmitted by said sample cell means into a plurality of wavelength constituents;

dispersive means for analysis of said polychromatic light transmitted by said sample cell means into a plurality of wavelength constituents;

aperture means and means for transmitting sequentially selected said wavelength constituents through said aperture means;

retro-reflective means for redirecting said selected wavelength constituents back through ~~said~~ aperture means and said sequential transmitting means and said dispersive means whereby said selected wavelength constituent is double dispersed;

means for separating said double dispersed selected wavelength constituents from unreflected radiation;

single detector means responsive to said double dispersed selected wavelength constituents reflected from said retro-reflective means for generating a time dependent signal containing the absorbance information for each said wavelength constituent;

means for deriving from said time dependence of said signal said absorbance information for each said wavelength constituent; and

means for recording said information.

7. The apparatus of claim 6 further comprising means for directing another portion of light from said light source means through another sample cell means and means for sequentially presenting said portion and said another portion to said dispersing means.

8. The apparatus of claim 7 further comprising means for comparing a portion of said time-dependent signal corresponding to one said selected wavelength constituent of said portion of light transmitted through said sample cell means with another portion of said time-dependent signal corresponding to one said selected wavelength constituent of said another portion of light transmitted through said another sample cell means.

9. The apparatus of claim 8 including comparison means for comparing said portion of said time-dependent signal with said another portion of said time-dependent signal whereby a sample reference comparison is achieved.

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